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Solubilities of hydroxybenzaldehyde isomers and their mixture in subcritical 1,1,1,2-tetrafluoroethane

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ABSTRACT

The static flow method coupled with gas chromatography analysis was used to measure the solubilities of pure 4-hydroxybenzaldehyde, 3-hydroxybenzaldehyde and their mixture with equal molar ratio in subcritical 1,1,1,2-tetrafluoroethane (R134a) at 308, 318, 328 K and 5.0–15.0 MPa. Comparison of the solubility of each solute in the binary subcritical R134a system with that in the ternary system was made. Furthermore, the effect of molecular structure on the solubility was discussed, and the improvement effect factor (μ) and separation factor (SF) of each solid solute in the ternary system had been investigated. In addition, the solubility enhancement factor (δ) had been defined and calculated to compare the solubility of the same solute in subcritical R134a with that in supercritical carbon dioxide. The solubility data of pure solute in the binary subcritical R134a system were correlated by Chrastil and Méndez-Santiago and Teja (MST) models, while the solubility data in the ternary system were correlated by their modified models (Chrastil-G and MST-S), Sovová and its modified models. All the calculated solubility data showed satisfactory agreements with the experimental one.

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1. Introduction

In the past several years, subcritical and supercritical fluids have been very active in both theoretical research and practical application fields because of their low surface tension, high diffusivity, low viscosity, and high compressibility [1]. To our best knowledge, solubilities of a large number of low-volatility and polar substances in subcritical and supercritical fluids have been measured, reported, and reviewed [2–6]. To overcome the deficiency of supercritical carbon dioxide (SCCO$_2$) in the dissolving capacity, which limits its developments in separation, reaction and material preparation processes because of its non-polarity, many researchers have focused on the alternative solvent 1,1,1,2-tetrafluoroethane (R134a) [7–9].

As a hot-spot study among the extraction solvents, R134a is non-flammable and nontoxic and has zero ozone depletion potential. Thus, R134a has been considered as a chlorofluorocarbon replacement and is widely used in refrigeration and auto air conditioning systems. The critical temperature and pressure of R134a are 374.2 K and 4.06 MPa, respectively, so it can be used as a more suitable solvent with better dissolving capacity for polar solid solute at much lower pressure than SCCO$_2$, whose critical pressure is 7.38 MPa.

Furthermore, its dipole moment is 2.1 Debye, which is much more than that of SCCO$_2$ (zero Debye) [10], and there is no residual solvent in the product because of its boiling point (246.9 K) well below the ambient temperature. But so far, the study on the solubility of organic solutes in subcritical R134a is comparatively rare [11,12]. Without any doubt, there is a need for measuring the solubility of more compounds in subcritical R134a to propose the optimal operation condition for subcritical fluid extraction process.

4-Hydroxybenzaldehyde (4-HBA) is an important intermediate for producing fine chemicals and is extensively used in perfume, medicine, agrochemical and cosmetic industries. For example, it is a typical substance of vanilla bean extracts [13]. 3-Hydroxybenzaldehyde (3-HBA), as the isomer of 4-HBA, is a raw material for many chemical and pharmaceutical syntheses, such as the preparation of new anticancer, antidiabetic drugs and fire-resistant resin compositions [14]. The main reason why we choose these two materials is that it is difficult to separate them by conventional separation technology because they are isomers. First, they have similar melting temperatures, which are 388–391 K for 4-HBA [15] and 376–378 K for 3-HBA [16], so it is difficult to separate them by melting and crystallization. Second, though the difference between their boiling temperatures, which are 583 K for 4-HBA [17] and 513 K for 3-HBA [18], is large, it is not economical to separate them by evaporation at high temperature and crystallization. Lastly, they have similar solubility in traditional solvents like water,

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Table 1
Details of the compounds.

Compound	Formula	CAS registry no.	Mass purity[a] (%)	Source
4-Hydroxybenzaldehyde	$C_7H_6O_2$	123-08-0	≥98.0	Aladdin Chemistry Co. Ltd.
3-Hydroxybenzaldehyde	$C_7H_6O_2$	100-83-4	≥97.0	Aladdin Chemistry Co. Ltd.
1,1,1,2-Tetrafluoroethane	$C_2H_2F_4$	811-97-2	≥99.9	DuPont Company
Anhydrous ethanol	C_2H_6O	64-17-5	≥99.7	Beijing Chemical Reagent Factory
High purity nitrogen	N_2	7727-37-9	≥99.999	Beijing Praxair Industrial Gas Co. Ltd.

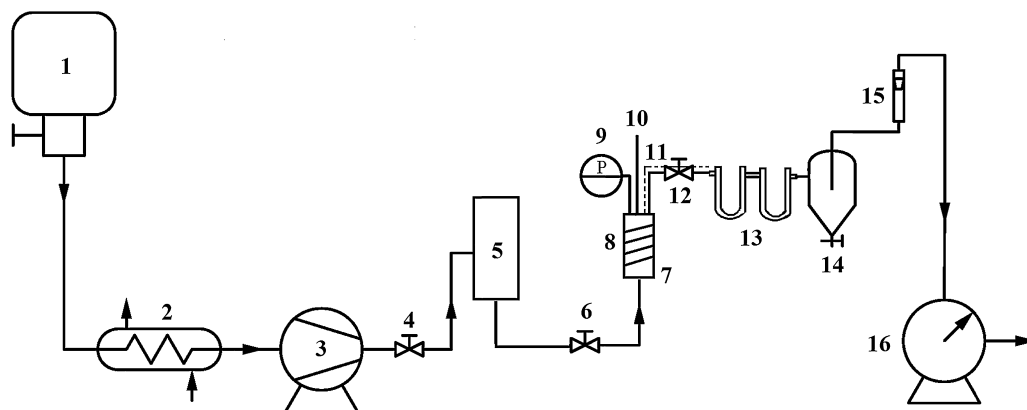[a] The mass purity was stated by the supplier.

Fig. 1. Schematic diagram of the experimental apparatus for static method.

ethanol, ether, acetone and benzene, so it is difficult to separate them according to their solubility. On the other hand, the solubility of 4-HBA, 3-HBA and their mixture in subcritical R134a has never been reported so far, so this work would enrich the solubility data of isomers in subcritical R134a. At last, this work will help to investigate how the position of the functional groups influences the solubility of each solute and is one part of our long-term objective to investigate the solubility behavior of solutes in supercritical or subcritical fluids by analyzing the effects of different varieties and positions of functional groups on the benzene ring.

Taking the aspects talked above into account, the solubilities of 4-HBA, 3-HBA and their mixture with equal molar ratio in subcritical R134a were measured by the static method. The temperature ranged from 308 to 328 K, and the pressure ranged from 5.0 to 15.0 MPa. The experimental data were discussed according to the chemical structure and related properties. At last, the semiempirical models of Chrastil, Méndez-Santiago and Teja (MST), and their modified models as well as Sovová and its modified models were applied to correlate to the solubility data that we obtained.

2. Experiment

2.1. Materials

Table 1 lists the CAS registry No., formula, mass purity and source of the compounds that were involved in this work. All the chemicals were used without further purification.

2.2. Apparatus and procedure

The apparatus for static method was implemented to determine the solubility of 4-HBA, 3-HBA and their mixture with equal molar ratio in subcritical R134a, and a detailed description of the apparatus and experimental procedure was given in our previous work [19]. A schematic diagram of the static apparatus is presented in Fig. 1. A high-pressure equilibrium cell with an effective volume of 10 mL was the major apparatus. The uncertainty of the measured

temperature and pressure in the cell was ±0.1 K and ±0.2 MPa, respectively.

R134a cylinder was inverted so that the liquid R134a could be introduced into the refrigerating machine (Zhengzhou Great Wall S&T. Co., LTD, model DLSB 10/40) and then flowed into the constant-flux pump (Dongtai Yanshan Instrument Factory, model BLH-1040), where R134a was compressed to the experimental pressure. Through the entry control valve, R134a entered into the surge flask, and then the exit control valve was used to introduce R134a into the equilibrium cell, which was wrapped with heating band to control the experimental temperature. Both ends of the equilibrium cell are metal membranes in order to prevent entrainment. Before each experiment, 3–4 g solid solute was loaded into the cell and the air in the equilibrium cell was discharged by blowing a little low pressure R134a. The contact state of solute and subcritical R134a in the equilibrium cell were maintained for at least 60 min at the experimental temperature and pressure. The saturated subcritical R134a was then vented from the top of the equilibrium cell and depressurized into atmospheric pressure through a decompression sampling valve, which was wrapped with a heating coil to avoid being blocked by the precipitated solid solute. Finally, the solute was separated from the gaseous R134a and gathered in the two connected U-shape tube for analysis by the gas chromatography. The volume of R134a was calculated by the wet gas flow meter with an uncertainty of ±0.01 L.

2.3. Preparation

To ensure the reliability of the apparatus, experiments had been done to determine the equilibrium time and analyze the experimental data repeatability, and the experimental results were shown in Fig. 2. From Fig. 2, it can be found that when the experimental time is more than 45 min, the solubility almost remains the same. By combining the theoretical optimal equilibrium time and experimental efficiency into consideration, the experimental time was decided to be 60 min for all the experimental conditions.

In this work, each reported datum was an average of at least three replicated sample measurements with error between each